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# THE DIMESITYLBORON GROUP IN ORGANIC CHEMISTRY. 6

## HYDROBORATIONS WITH DIMESITYLBORANE.

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Dimesitylborane, 1, is a readily available, solid, stable borane that is the most selective known reagent for the regioselective hydroboration of unsymmetrical alkynes. In addition *all*-alkynes are selectively hydroborated compared with even terminal alkenes. The hydroboration of alkenes with 1 is slow and sensitive to steric factors, thus giving promise of good selectivity between different types of alkene.

As well as allowing their production, the dimesitylboron group stabilises adjacent carbanions,[1] which undergo a variety of reactions of great synthetic potential.[2,3] The group also acts to confine electrophilic attack on a substituted allyl carbanion to the $\gamma$- position, so giving rise to substituted *trans*-alkenylboranes, which have a rich chemistry.[4] It is therefore important to introduce the dimesitylboron group without the use of organometallics so that a wide variety of functional groups can be tolerated. We therefore decided to investigate the hydroborating properties of dimesitylborane ($Mes_2BH$) 1, which though a known compound[5] had never been tested for this purpose. In our hands the reported preparation[5] was so capricious as to be useless in practise. However reduction of fluorodimesitylborane with a solution of lithium aluminium hydride in glyme (eq.1) readily gives 1, m.p. 68°C in 70% recrystallised yield. *Dimesitylborane is now a readily available solid borane.*

$$4\ Mes_2BF + LiAH_4 \longrightarrow LiF + AlF_3 + \underset{1}{4Mes_2BH} \qquad (1)$$

Dimesitylborane is stable *and readily weighed out in air without loss of hydride activity.* It is poorly soluble, and in THF, the best ethereal solvent, a saturated solution is only 0.15M. Over six days at room temperature such solutions showed no sign of dismutation and did not change molarity and were used for kinetic runs. For preparative reactions the use of suspensions of 1 is satisfactory, particularly as disappearance of the solid is a visual indication of completion of reaction. Dimesitylborane is a dimer,[5] but for convenience we use the monomeric formula. The borane 1 readily reacts with lithium hydride[5]

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to give lithium dimesitylhydroborate 2 which is a very stable solid. Reaction of 2 with benzyl chloride gives 1 and lithium chloride and the suspension can be used efficiently and directly for hydroboration.

The results of the hydroboration of alkenes are presented in Table 1.

Table 1.

Hydroboration/oxidation of alkenes with $Mes_2BH$ in THF

| Exp. | Alkene | Temp ($^oC$) | Time(h) | %Reaction | Products | Ratio | Yields[a] |
|---|---|---|---|---|---|---|---|
| 1 | Oct-1-ene | 25 | 8 | 100 | Octan-1-ol )<br>Octan-2-ol ) | 97<br>3 | 95 |
| 2 | " | 65 | 4 | " | " | " | " |
| 3 | Hex-1-ene | 25 | 8 | 97 | Hexan-1-ol )<br>Hexan-2-ol ) | 96<br>4 | 96 |
| 4 | " | 65 | 4 | " | " | " | 97 |
| 5 | 2,4,4-Trimethylpent-1-ene | 25 | 24 | 30 | 2,4,4-Trimethyl pentan-1-ol | - | 30 |
| 6 | " | 65 | 24 | 71 | " | - | 70 |
| 7 | *cis*-Pent-2-ene | 25 | 24 | 8 | Pentan-2-ol | - | 6 |
| 8 | " [b] | 65 | 24 | 100 | Pentan-2-ol)<br>Pentan-3-ol) | 76<br>24 | 90 |
| 9 | Styrene | 25 | 24 | 25 | 2-Phenylethanol | - | 18 |
| 10 | " | 65 | 24 | 80 | 2-Phenylethanol )<br>1-Phenylethanol ) | 99<br>1 | 80 |
| 11 | Cyclohexene | 25 | 24 | 10 | Cyclohexanol | - | 6 |
| 12 | " | 65 | 24 | 20 | " | - | 15 |
| 13 | 4-Vinylcyclohexene | 25 | 24 | 40 | 2(3-Cyclohexenyl) ethanol | - | 40 |
| 14 | " | 65 | 24 | 70 | " | - | 70 |

a) Yields are of total product estimated by g.c. by direct comparison with authentic samples. b) No pentan-1-ol could be detected.

The hydroborations are slow unlike those of diphenylborane,[6] and very sensitive to steric factors. Thus simple monosubstituted alkenes require 8h. for complete reaction at 25°C (Table 1, exp. 1,3) but a branching at C-3 causes a marked diminution in the rate of reaction (Table 1, exp. 13, 14). *cis*-Pent-2-ene requires 24h. at 65°C for complete reaction (an index incidentally, of the stability of 1 in great contrast to diphenylborane[6]) (Table 1, exp. 7,8). The *trans*-isomer is even slower. For a 2,2-disubstituted alkene even 24h. at 65°C leads to 70% reaction only (Table 1, exp. 6),whilst cyclohexene is hydroborated with the greatest difficulty (Table 1, exp. 11,12). The reaction with styrene is governed by steric factors and boron is placed almost exclusively (99%) on the terminal carbon (Table 1, exp. 13).

The differences in reactivity of different alkenes are very promising for carrying out selective hydroborations in molecules containing more than one double bond. We had expected that heating might give rise to complications due to retrohydroboration - hydroboration sequences. Fortunately this was not the case at 65°C (Table 1, exp. 8, note b).

In contrast to the reactions with alkenes, **1** mono-hydroborates alkynes with great ease. The results are presented in Table 2.

Table 2. Hydroboration/oxidation[a] of alkynes using $Mes_2BH$

| Experiment | Alkyne | Time (mins)[b] | Product(s) | Ratio | Yield[c] (%) |
|---|---|---|---|---|---|
| 15 | HexC⋮CH | 5 | Hept.CHO | - | 95 |
| 16 | PrC⋮CMe | 10 | BuCOMe )<br>PrCOEt ) | 90<br>10 | 96 |
| 17 | EtC⋮CEt | 5 | PrCOEt | - | 100 |
| 18 | PhC⋮CH[d] | 30 | $PhCH_2CHO$ | - | 85 |
| 19 | PhC⋮CMe | 60 | $PhCH_2COMe$ )<br>)<br>$PhCOCH_2Me$ ) | 98<br><br>2 | 94 |

a) Oxidation with $NaH_2PO_4$ buffered $H_2O_2$. b) Time for complete reaction of equimolar proportions of 0.1M $Mes_2BH$ in THF at 25°C with neat alkyne. c) G.c. yield of total product. d) $Mes_2BCH\overset{t}{:}CHPh$, m.p. 144-146°C isolated in 78% yield and fully characterised.

The products of hydroboration can be oxidised to the corresponding carbonyl compounds in excellent yield and it is the yields based on both reactions that are given in Table 2. The hydroboration itself seems to be essentially quantitative. The aldehydes were readily separated as the 2,4-D.N.P.'s in good yields (e.g. 2,4-D.N.P. of octaldehyde, m.p.104-106°C, 82% isolated yield). Dialkyl- and monoalkylalkynes hydroborate within 10m. but the rate is slowed somewhat by a phenyl group attached to the triple bond (Table 2, exp. 18, 19). Most noteworthy are the results with unsymmetrical disubstituted alkynes (Table 2, exp. 16, 19). If these results are compared with those obtained with other hydroborating agents (Table 3) it is clear that dimesitylborane is the most selective known reagent for the hydroboration of unsymmetrical alkynes.

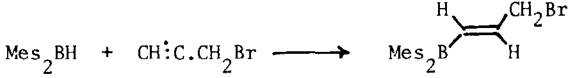
Table 3.

Selectivity of hydroboration of unsymmetrical alkynes.

| Hydroborating agent | $Pr^nC$ : | CMe | PhC : | CMe |
|---|---|---|---|---|
| $B_2H_6$ | 40 | 60[a,b] | 74 | 26 |
| $Sia_2BH$ | 39 | 61 | 19 | 81 |
| $Cx_2BH$[c] | 34 | 66 | 29 | 71 |
| $HBBr_2.SMe_2$ | 25 | 75 | 64 | 36 |
| 9-BBN | 22 | 78 | 65 | 35 |
| $Mes_2BH$ | 10 | 90 | 2 | 98 |

a) All analyses by g.c. examination of ketones resulting from oxidation of hydroboration products. b) The figures under each carbon atom give the percentage placement of boron on that atom. c) Cx=cyclohexyl.

The great differences between the rates of reactions with alkenes and alkynes suggest that any alkyne could be hydroborated by **1** in the presence of any type of alkene. Hence competition reactions for **1** were run between both oct-1-yne and hex-3-yne and the terminal alkene, oct-1-ene. In both cases there was complete reaction of the alkyne and zero reaction of the alkene! We are not certain of the properties of **1** as a reductant, though it is known that after 8h. at 0° reduction of cycloalkanones is incomplete,[5] but it is significant that propargyl bromide is quantitatively hydroborated by **1** to give the corresponding bromine containing borane (eq. 2).* Furthermore diphenylborane does not reduce esters and we expect **1** to be even more sluggish.



$$Mes_2BH + CH{\vdots}C.CH_2Br \longrightarrow Mes_2B(H)C{=}C(H)CH_2Br \qquad (2)$$

Thus **1** is highly chemoselective as well as steroselective in its reactions and should find wide synthetic application.

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